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RESEARCH ARTICLE

THEORETICAL EXPLANATION FOR CATALYTIC HYDROSILYLATION OF SOME ORGANIC MOLECULES MEDIATED BY A PHOSPHORUS DICATION COMPOUND

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ABSTRACT

Catalysis reactions under metal-free and ambient conditions have received great interest in terms of economic and environmental issues. Especially, the applications of Lewis acids for the processes are having special interest due to their unique roles in a huge number of organic reactions. In this sense, a recent compound PIII dication has played an important role in the catalytic hydrosilylation of carbonyls and olefins. Herein theoretical calculations were carried out to elucidate the mechanisms of the experimentally reported and unknown reactions. The proposed mechanisms show that the reactions of **a-d** can occur spontaneously, whereas the formation of pyridine has an endergonic nature.

Keywords: DFT, catalysis, Phosphorus, Reaction mechanism

1. INTRODUCTION

Lewis acids have become an important class of inorganic chemistry since the exploration of their breakthrough properties in terms of intriguing behaviors as catalysts towards several chemical transformations [1]. The compounds of BF_3, $AlCl_3$, $[CPh_3]^+$, and $[SiEt_2]^{2+}$ are examples of neutral and cationic Lewis acids with considerable acidity from the vacant *p* orbitals on central atoms [2-9]. Additionally, PV cations are also commonly used Lewis acids as catalysts for several reactions such as hydrogenations, polymerizations, hydrosilylations, and hydro-defluorinations [10-13]. Alternatively, PIII compounds are known to behave as Lewis bases due to their electron-donating properties in coordination and catalysis chemistry [14]. Indeed, the right coordination of PIII compounds can also be described as phosphenium dications with impressive Lewis acid character [15-17]. Of broad interest have been devoted to understand the attractive reactivity of PIII dications. In recent studies a number of reactions exemplified by PIII acceptors. The reactivity of PIII dications toward activation of C-F bond and hydride abstraction from silanes were shown by the Vidovic group [18-19]. Stephan group reported several PIII dications with different properties in terms of reactivity depending on the ligand systems [20-21]. In this regard, C-F bond activations of fluoroalkenes and CF_3 substituted species were reported by Stephan et al. Same group also systematically studied catalytic hydrosilylation reactions of carbonyls and olefins by PIII dication with terpyridine ligand [22]. The fluorophosphonium cation-promoted reaction mechanisms for catalytic reactions, including the hydrosilylation of olefins, have been investigated in detail in terms of experimental and theoretical aspects [23-25]. The reports pertaining to the studies conclude a key intermediate that stems from hydride abstraction or heterolytic cleavage of H_2.

Previous findings pertaining to the role of fluorophosphonium cations in hydrosilylation reactions suggest the formation of a fluoro–hydrido–phosphorane compound as a key intermediate [26]. This formation can be expressed in two manners; direct hydride abstraction of phosphorus cation from a silane or splitting of H_2 in frustrated Lewis pair. Although the key intermediate could not be determined experimentally, the detailed DFT calculations suggest its energetically plausible appearance. This

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situation may stem from the strong hydridic nature of the key intermediate. To the best of our knowledge, however, there is no DFT study on the mechanism of catalytic cycle of PIII dications. Herein, we would like to address potential reaction mechanisms involving hydrosilylation of several organic compounds by a phosphorus PIII dication, $[(\text{terpy})\text{PPh}]^{2+}$.

2. COMPUTATIONAL DETAILS

Gaussian 16 package program was applied to all calculations in this study [27]. For optimizations of the dicationic structures in the gas phase, Becke’s three-hybrid method and the exchange functional of Lee, Yang, and Parr (B3LYP) theory was used with the split valence polarization basis set of def2-SVP [28,29]. The Becke-Jonson (BJ) damping with D3 dispersion correction function was included in all the calculations [30]. In order to characterize the optimized structures as minima or transition state, the frequency calculations were considered. The Gibbs free energies in kcal mol^{-1} are given in the entire text. Additionally, the intrinsic reaction coordinate (IRC) calculations were performed to confirm the relevant transition states by determining their routes to correct local minimas. For this, the second-order Gonzalez-Schlegel method was considered [31,32]. For the preparation of Figure 1 and visualization of the structures, the GaussView 5.0 program was used [33].

2. RESULTS and DISCUSSION

In 2019, the Stephan group accomplished hydrosilylation of some organic molecules under mild conditions mediated by a PIII dication compound, $[(\text{terpy})\text{PPh}]^{2+}$ [22]. With this incentive, we have proposed reaction mechanisms for hydrosilylation of **a-e** by a PIII dication by following hydride abstraction from triethylsilane in Figure 1.

In the case of **a**, the first step yields the intermediate **1a** which consists of $[\text{Ph-P-H}]^+$ and 3-methyl-3-(triethylsilyl)butan-2-ylium subunits via **TS1a** by an energy barrier of $\Delta G^{\neq} = 19.5$ kcal mol^{-1} (Figure 1). Furthermore, the generation of **1a** is found to be slightly endergonic by 4.4 kcal mol^{-1}. The energy barrier and slight endergonicity can be acceptable for a reaction that occurs at 50 ºC. It is also noteworthy that the formation of the potential intermediate **1a** manifests the highest energy barrier and only endergonic first step. Subsequently, the hydride abstraction from $[\text{Ph-P-H}]^+$ moiety by butan-2-ylium to yield **2a** possess a relatively lower energy barrier of $\Delta G^{\neq} = 13.6$ kcal mol^{-1} for **TS2a** compared to that of first step. The calculated total energy of the reaction is $\Delta G = -6.3$ kcal mol^{-1}.

Table. Relative energies of the proposed reaction mechanisms of **a-e** at the B3LYP-D3(BJ)/def2-SVP level of theory. Energies are in kcal mol^{-1}.

	a	**b**	**c**	**d**	**e**
a-e→TS1(a-e)	19,6	9,0	11,5	5,8	6,1
TS1(a-e) →1(a-e)	14,9	17,1	16.4	29.5	28.1
1(a-e) →TS2(a-e)	13.6	12.7	19.8	20.4	26.0
TS2(a-e)→2(a-e)	25.6	28.4	61.4	13.7	9.2
Overall Energy	-6.3	-17.5	-51.5	-13.5	8.3

In the second part, we have investigated the energy profile of the stepwise hydrosilylation of acetone (**b**). In a similar manner, the first step is associated with the hydride abstraction by PIII dication via **TS1b**. The required energy ($\Delta G^{\neq} = 9.0$ kcal mol^{-1}) to arrive at **TS1b** is calculated to be strongly lower than that for **TS1a**. The second step estimates the hydride abstraction via **TS2b** by an energy barrier of $\Delta G^{\neq} = 12.7$ kcal mol^{-1} and the overall energy for **2b** is dedicatedly exergonic ($\Delta G = -17.5$ kcal mol^{-1}).

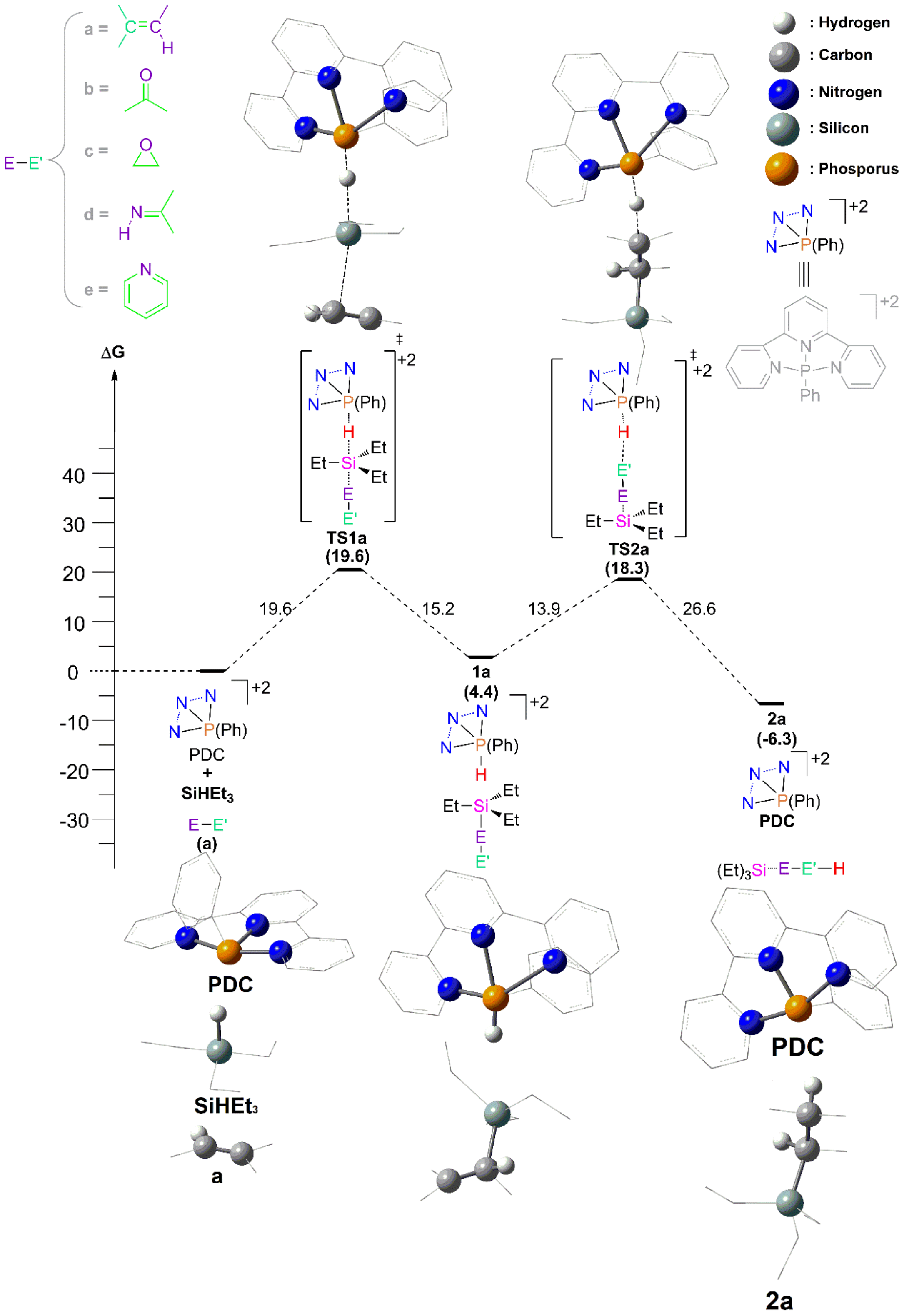

Figure 1. General representation of the proposed reaction mechanism for the formation of **2a-2e** at the B3LYP-D3(BJ)/def2-SVP level of theory. The relative energies and structures are given considering formation of **2a**. (PDC = Phosphorus dication)

Alternatively, we have also considered hydrosilylation of the simplest epoxide (**c**), ethylene oxide, as another oxygen-containing system for comparison with acetone. In a similar fashion, the nucleophilic attack from the oxygen center to the silicon center of triethylsilane to form oxiranium intermediate **1c** proceeds via **TS1c**. This step needs to overcome a slightly higher energy barrier of $\Delta G^{\neq} = 11.5$ kcal mol^{-1} as compared to that of acetone analogue (**TS1b**). The subsequent ring-opening of the resulting oxiranium **1c** to give ethoxytriethylsilane **2c** product has the strongest exergonic nature ($\Delta G^{\neq}= -51.5$ kcal mol^{-1}), albeit with a substantial barrier of $\Delta G^{\neq} = 19.8$ kcal mol^{-1}.

As for the hydrosilylations of nitrogen containing systems imine (**d**) and pyridine (**e**), the calculations depict that the lowest energy barriers are determined to form intermediates **1d** and **1e** via **TS1d** and **TS1e** with $\Delta G^{\neq} = 5.8$ kcal mol^{-1} and $\Delta G^{\neq} = 6.1$ kcal mol^{-1}, respectively. Furthermore, the strongest exergonic characters are appeared for **1d** and **1e** in comparison with other studied molecules by $\Delta G^{\neq} = 29.5$ kcal mol^{-1} and $\Delta G^{\neq} = 28.1$ kcal mol^{-1}, respectively. In stark contrast to the initial energy barriers of **TS1d** and **TS1e**, the second steps to yield target compounds **2d** and **2e** via **TS2d** and **TS2e** have the highest energy barriers by $\Delta G^{\neq} = 20.4$ kcal mol^{-1} and $\Delta G^{\neq} = 26.0$ kcal mol^{-1}. For the sake of comparison, the yielding of the hydrosilylated compounds **2d** and **2e** exhibits different thermochemical properties. Taking account of the endergonic nature of hydrosilylation of pyridine, the structure **2e** is not able to be furnished spontaneously. Otherwise, the higher backward energy barrier to **TS2d** makes the formation of **2d** more facile than **TS2e**.

2. CONCLUSION

Collectively, we have described possible reaction mechanisms for the hydrosilylation of **a-e**. In all cases, the key intermediates of **1a-1e,** similar to the fluoro–hydrido–phosphorane observed from fluorophosphonium, are tracked and play an important for determining the nature of the reactions. All the proposed reaction mechanisms of **PDC** with **a-e** proceed in stepwise manners to afford the hydrosilylated products **2a-2e**. The only endergonic character is observed for hydrosilylation of pyridine **e**. Depending on the thermochemical data, conversely, we suggest that another nitrogen-containing system, imine, is found to be the most reactive toward silane due to the lowest initial energy barrier.

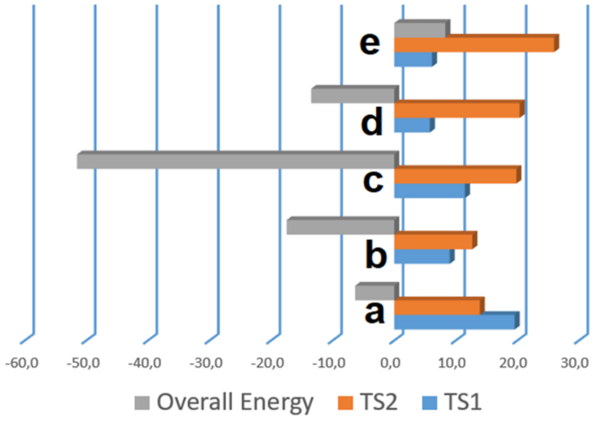

Figure 2. Graphical visualization of the energy barriers to arrive at **TS1a-TS1e** and **TS2a-TS2e** and overall energies for **2a-2e**.

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CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

REFERENCES

[1] Sereda O, Tabassum S, Wilhelm R. Asymmetric Organocatalysis. Berlin, Heidelberg, Germany: Springer Berlin Heidelberg, 2009.

[2] Dagorne S, Wehmschulte R. Recent developments on the use of group 13 metal complexes in catalysis. Chem Cat Chem 2018; 10: 2509-2520.

[3] Shen Q, Huang YG, Liu C, Xiao JC, Chen QY, Guo Y. Review of recent advances in C-F bond activation of aliphatic fluorides. J Fluor Chem 2015; 179: 14–22. doi: 10.1016/j.jfluchem.2015.07.007

[4] Douvris C, Nagaraja CM, Chen CH, Foxman BM, Ozerov OV. Hydrodefluorination and other hydrodehalogenation of aliphatic carbon-halogen bonds using silylium catalysis. J Am Chem Soc 2010; 132: 4946–4953.

[5] Douvris C, Ozerov OV. Hydrodefluorination of perfluoroalkyl groups using silylium-carborane catalysts. Science, 2008; 321, 1188-1190.

[6] Stahl T, Klare HFT, Oestreich M. Main-group lewis acids for C–F bond activation. ACS Cat 2013; 3: 1578–1587.

[7] Ahrens M, Scholz G, Braun T, Kemnitz E. Catalytic hydrodefluorination of fluoromethanes at room temperature by silylium-ion-like surface species. Angew Chem Int Ed 2013; 52: 5328–5332.

[8] Pan B, Gabbai FP. $[Sb(C_6F_5)_4][B(C_6F_5)_4]$: An air stable, lewis acidic stibonium salt that activates strong element-fluorine bonds. J Am Chem Soc 2014; 136: 9564–9567.

[9] Farrell JM, Hatnean JA, Stephan DA. Activation of hydrogen and hydrogenation catalysis by a borenium cation. J Am Chem Soc 2012; 134: 15728–15731.

[10] Terada M, Kouchi M. Novel metal-free Lewis acid catalysis by phosphonium salts through hypervalent interaction. Tetrahedron 2006; 62: 401–409.

[11] Caputo CB, Hounjet LJ, Dobrovetsky R, Stephan DW. Lewis acidity of organofluorophosphonium salts: Hydrodefluorination by a saturated acceptor. Science 2013; 341: 1374–1377.

[12] Zhu J, Perez M, Caputo CB, Stephan DW. Use of trifluoromethyl groups for catalytic benzylation and alkylation with subsequent hydrodefluorination. Angew Chem Int Ed 2016; 55: 1417–1421.

[13] Bayne JM, Stephan DW. Phosphorus lewis acids: emerging reactivity and applications in catalysis. Chem Soc Rev 2016; 45; 765–774.

[14] Fan YC, Kwon O. Advances in nucleophilic phosphine catalysis of alkenes, allenes, alkynes, and MBHADs. Chem Commun 2013; 49: 11588–11619.

[15] Burford N, Ragogna P. New synthetic opportunities using Lewis acidic phosphines. J Chem Soc Dalton Trans 2002; 4307–4315.

[16] Gudat D. A very peculiar family of N-heterocyclic phosphines: unusual structures and the unique reactivity of 1,3,2-diazaphospholenes. Dalton Trans 2016; 45; 5896–5907.

[17] Slattery JM, Hussein S. How Lewis acidic is your cation? Putting phosphenium ions on the fluoride ion affinity scale. Dalton Trans 2012; 41: 1808–1815.

[18] Dorevic N, Tay MQY, Muthaiah S, Ganguly R, Dimic D. C–F bond activation by transient phosphenium dications. Inorg Chem 2015; 54: 4180–4182.

[19] Dorevic N, Ganguly R, Petkovic M, Vidovic D. E–H (E = B, Si, C) Bond activation by tuning structural and electronic properties of phosphenium cations. Inorg Chem 2017; 56: 14671–14681.

[20] Chitnis SS, Krischer F, Stephan DW. Catalytic hydrodefluorination of C-F bonds by an air-stable PIII lewis acid. Chem Eur J 2018; 24: 6543-6546.

[21] Chitnis SS, LaFortune JHW, Cummings H, Liu LL, Andrews R, Stephan DW. Phosphorus coordination chemistry in catalysis: Air stable P(III)-dications as lewis acid catalysts for the allylation of C-F bonds. Organomet 2018; 37: 4540-4544.

[22] Andrews RJ, Chitnis SS, Stephan DW. Carbonyl and olefin hydrosilylation mediated by an air-stable phosphorus(III) dication under mild conditions. Chem Commun 2019; 55: 5599-5602.

[23] Pérez M, Hounjet LJ, Caputo CB, Dobrovetsky R, Stephan DW. Olefin isomerization and hydrosilylation catalysis by lewis acidic organofluorophosphonium salts. J Am Chem Soc 2013; 135; 18308–18310.

[24] Pérez M, Qu ZW, Caputo CB, Podgorny V, Hounjet LJ, Hansen A, Dobrovetsky R, Grimme S, Stephan DW. Hydrosilylation of ketones, imines and nitriles catalysed by electrophilic phosphonium cations: Functional group selectivity and mechanistic considerations. Chem Eur J 2015; 21; 6491–6500.

[25] Vom Stein T, Perez M, Dobrovetsky R, Winkelhaus D, Caputo CB, Stephan DW. Electrophilic fluorophosphonium cations in frustrated Lewis pair hydrogen activation and catalytic hydrogenation of olefins. Angew Chem Int Ed 2015; 54: 10178–10182.

[26] Kostenko A, Dobrovetsky R. The role of the fluoro–hydrido–phosphorane intermediate in catalytic hydrosilylation of acetophenone: Computational study. Eur J Org Chem 2019; 318–322.

[27] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson, GA, Nakatsuji, H, Li X, et al. Gaussian 16, Revision B.01, Gaussian Inc: Wallingford CT., 2016.

[28] Lee C, Yang W, Parr RG. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. Phys Rev B, 1988; 37: 785-789.

[29] Weigend F, Ahlrichs R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys Chem Chem Phys 2005; 7: 3297-305.

[30] Grimme S, Ehrlich S, Goerigk L. Effect of the damping function in dispersion corrected density functional theory. J Comp Chem 2011; 32: 1456-1465.

[31] Gonzalez C, Schlegel HB. Improved algorithms for reaction path following: higher- order implicit algorithms. J Chem Phys 1991; 95: 5853-5860.

[32] Wiberg KB. Application of the pople–santry–segal CNDO method to the cyclopropylcarbinyl and cyclobutyl cation and to bicyclobutane. Tetrahedron 1968; 24: 1083-1096.

[33] Dennington RII, Keith T, Millam J, Eppinnett K, Hovell WL, Gilliland R. GaussView v.5.0.9 Visualizer and Builder. Gaussian Inc. Wallingford CT., 2009.